SOME CONSIDERATIONS ON THE STRUCTURE AND RADIATION CHEMISTRY OF WATER

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ABSTRACT. The variation in the yield of radiolytic products
with higher ranges of concentration and with the temperature
unexplained as yet by the radical diffusion theory is dis-
cussed. It is shown that by considering some structural
features of water, both the temperature dependence of the
radical yield and the concentration dependence of H_2 pro-
duction in the entire range of concentration can be inter-
preted. The results predicted from the relationships thus
established agree to orders of magnitude with the measured
temperature coefficients of radical yields. Finally some
problems concerning the scope of the radical diffusion
model are considered.

Summary

The yield of the products of the radiolysis of aqueous solutions is affected
by the temperature and, in the case of higher concentrations, also by the con-
centration of the solution in a manner not yet clarified on the basis of the
theory of radical diffusion. We intend to demonstrate here that, by considera-
tion of the peculiarities of the water structure, both the temperature dependence
of the yields of radicals and the concentration dependence of the H_2 yield can
be interpreted over the entire concentration range. The calculations made on
the basis of the relationship established and the measured values of the tem-
perature coefficients of the yields of radicals show agreement within one order
of magnitude. Indications are given as to some problems of the validity limit
of the theory of radical diffusion.

1. Introduction

Substantially, the theory of radical diffusion yields a correct quantita-
tive description of the radiative chemical processes taking place in aqueous
solutions, but in its original form it is unsuitable for explaining some phe-
nomena. The effect of pH, temperature, isotope composition, and phase transi-
tion is given by the theory, in agreement with experience only if parameter
values are chosen that are not satisfactorily substantiated by the physical
interpretation serving as the basis for the theory (Ref.1). On the other hand,
the concentration dependence of the molecular H_2 yield also cannot be interpreted
by the theory over the entire concentration range (Ref.2). In one of our earlier
works (Ref.3, 4), we demonstrated that a physically reasonable change can be

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* Numbers in the margin indicate pagination in the foreign text.

performed on this model, by which - while retaining the basic concept unchanged - the influence of the variation in pH on the primary processes can be interpreted. In this work, attempts have been made to further develop the model used as a basis of the radical diffusion theory in such a manner as to render it also suitable for an interpretation of the effect of the temperature and of the concentration dependence of the H_2 yield. In this study, the variations in yield caused by phase transition will be treated as empirical data. The general judgment concerning the basic hypotheses of the radical diffusion theory is given briefly at the end of our paper, but the considerations touched upon in the first part of our article remain included in the field of the radical diffusion theory.

2. Summary of some Experimental Results

The results to be interpreted will be discussed briefly, together with those used only in our calculations.

Concentration dependence of the molecular H_2 yield. In dilute solutions, $G(H_2)$ decreases linearly with the cube root of the activity of the solute. According to measurements by Mahlman (Ref.6), this straight line shows a relatively sharp break in case of an activity of about 0.71 of the solution and then continues in a straight line of a more shallow slope. The cube root dependence in the case of γ-irradiation can be expected on the basis of the radical diffusion theory (Ref.7, 2), but the similar dependence occurring in a range of high concentration cannot be explained by the original model (Ref.2).

Effect of pH on the primary yields. The yields of radicals and the net water decomposition yield increase at decreasing pH effect. According to the theory of radical diffusion, this corresponds to a steadily less compact initial radical distribution at decreasing pH. As an explanation, it was assumed (Ref.3) that the electron capture of the H_3O^+ ions loosens the clusters.

Effect of temperature. The yield of the molecular decomposition products of water decreases with increasing temperature, and the radical yields increase (Ref.5). On the basis of the radical diffusion theory, no temperature effect is expected because the rising temperature causes the constants of both the reaction rate and diffusion to increase, and these exert an opposite effect on the yields.

Radical yields in irradiated ice. For ice irradiated at $4.2^\circ K$, a paramagnetic resonance spectrum characteristic of both the H atoms and the OH radicals has been demonstrated. The two radicals are formed with an approximately equal yield being $G_H = 0.9$, $G_{OH} = 0.8$ radicals/100 ev (Ref.8). In neutral ice, the H atoms are no longer stable above $4.2^\circ K$, but in frozen acid solutions they are identifiable also at $77^\circ K$ (Ref.9). Unfortunately, no measurements in acid solutions at $4.2^\circ K$ are known as yet.

3. Determination of Yields of Radicals in Water with a Structure

According to the theory of radical diffusion, water is a disordered

molecular cluster in which there are no pronounced directions, and no order can be detected in it even over short distances. In reality, however, water has a definite structure, and only by considering this structure can most properties of water be interpreted. Therefore, it seems to be highly probable that this structure plays a part also in the mechanism of radiolytic processes taking place in water.

Several detailed summaries of the extensive theoretical and experimental investigations on the detection of the water structure can be found in the literature (Ref.10, 11, 12). Here, only one or two points of the theory, of interest to us, will be discussed. The models of water structure can be divided into two groups: single-phase and multiphase models. According to the former, the hydrogen bridges between the water molecules extend throughout the system, and the partial disorder typical of the liquid state is caused by local distortions of the linkages or by rupture of certain bonds. The second group of theories postulates an order approaching the perfect order extending only to a few, or to some tens of water molecules, and imagines close-packed water molecules in mutual dipole interaction and in interaction with the clusters among those held together by hydrogen bonds and exhibiting an ice-like structure. According to experience, both models yield good results, which shows that both relatively well approach physical reality. Because of its simplicity, the multiphase model is used in our work.

Quite recently, Wada (Ref.13) developed a two-phase model on the basis of a phenomenologic thermodynamic theory, while Némethy and Scheraga (Ref.12) derived a five-phase model by a statistical mechanics method. Wada distinguishes in water only "close-packed" and "ice-like" parts, whereas Némethy and Scheraga, in addition to close-packed molecular groups, differentiate between molecule types linked by one-, two-, three-, and four-hydrogen bridges. The molecules forming the hydrogen bond are present in relatively large groups containing, on the average, 20 - 90 molecules. Although the group does not exhibit the ice-like structure, it still is of the ice-like type since the bonds are not distorted and since it contains the maximum possible number of four-coordination molecules. Between the groups and the close-packed water portions, steady rearrangement takes place, and the average lifetime of a group is 10^{-10} sec (Ref.14). The mole fraction of the bonded water molecules decreases slowly with increasing temperature.

Let us next study the formation of radical clusters in "two-phase water". One cluster is always formed as a primary ionization event in the ambient medium containing a few water molecules. Since the probability of ionization can be considered as proportional to the electron quotient, the probability of ionization of a molecule bonded in an "ice-like" group becomes equal to the γ-mole fraction of the water molecules in the "ice-phase". The majority of the radical reactions take place during the average lifetime of 10^{-10} sec of the group (Ref.15); in other words, from the viewpoint of the so-called physical and chemical threshold of radiative chemical conversion (this is the step determining the primary yields), the group can be considered as stable. The large difference between the radical yields of ice and water indicates that it is important for the formation of the cluster whether the radicals were formed in ice-like or close-packed water portions. Thus, in water at least two kinds of average clusters must be expected: one "ice-like" and one "non-ice-like" (close-

packed). The radical and molecular yields measured in water should therefore be considered as the weighted average of the two yields, where the weighting factor is the mole fraction of the water molecules found in the ice-like water portion. The primary yield of any product can thus be given by the following expression:

$$G = \gamma g^* + (1-\gamma)g \qquad (1)$$

where G is the measured average yield, g^* is the yield of radiolysis from the ice-like cluster, and g is the yield of radiolysis obtained from a "close-packed" cluster.

Concentration dependence of the molecular H_2 yield. The result described in the Introduction (Ref.6) can be interpreted as follows by means of a model of "two-phase irradiated water": In the case of using γ-irradiation, the theory of radical diffusion shows rather accurately the cube root concentration dependence of the molecular yield (Ref.2, 7). However, in the Ganguly-Magee theory (Ref.16) used as a basis for these calculations, the concentration of the solution never appears alone but always as the $k_s t_0 c_s$ product, where k_s is the rate constant of the reaction between the radical and the solute, c_s is the concentration, t_0 is the time factor characterizing the size of the cluster. The result of the numerical calculations based on the theory can thus be given approximately by the relationship

$$G(H_2) = a - b\left(k_s t_0 c_s\right)^{1/3} \qquad (2)$$

in other words, by plotting $G(H_2)$ as a function of $c_s^{1/3}$ a straight line is obtained whose slope is proportional to $(k_s t_0)^{1/3}$.

The low yield of radicals measured in ice suggests that the clusters formed in an ice-like structure are more compact than those formed in the close-packed structure. Accordingly, two average clusters of different size and thus characterized by different t_0 must be expected, which requires obtaining $G(H_2)$ as the sum of two equations of the form of eq.(2). In graphical representation, this corresponds to two straight superpositions, in full agreement with Mahlman's experience.

Effect of pH on primary yields. It was demonstrated in one of our earlier works (Ref.3) that the pH dependence of the primary yields can be described by the following equation:

$$\bar{G} = x G' + (1-x)G \qquad (3)$$

where x is the probability of the electron capture of the H_3O^+ ions; its value increases with decreasing pH between 0 and 1. Here, G is the yield obtained in a neutral solution and G' that in a strongly acid solution. Considering also the structure of water, both G and G' can be given by equations of the type of eq.(1). Since the factor x is a function of the size of the clusters, eqs.(1) and (3) can be combined into the following equation

$$\bar{G} = \gamma\left[x^* g^{*\prime} (1 - x^*)g^*\right] + (1-\gamma)\left[x g' + (1-x)g\right] \qquad (4)$$

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where the symbols with an asterisk refer to the "ice-like" clusters, while the symbols with a prime refer to the strongly acid media.

For neutral water, i.e., at $x = x^* = 0$, eq.(1) is obtained, while for strongly acid solutions ($x = x^* = 1$) the following analogous equation

$$G' = \gamma g^{*'} + (1 - \gamma) g' \tag{5}$$

is obtained from eq.(4). Disregarding the fact that the probability of electron capture of the H_3O^+ ions depends on the cluster size, i.e., assuming that $x = x^*$, eq.(4) is transformed into eq.(3).

It can be seen that the forms of eqs.(1) and (3) are completely identical. The two weighting factors γ and x, however, differ considerably in their physical meaning. In water with a structure, two kinds of average clusters are formed with their numerical ratio given by γ. The simple yields g^* and g attributed to the various types of cluster really exist, and their combination according to γ has a physical meaning. On the other hand, the presence of H_3O^+ ions does not cause the appearance of a new cluster type, but uniformly affects the radical distribution of all clusters. Therefore, the separation of the G and G' elementary yields and their combination according to x can be considered only as a mathematical approximation [see also (Ref.3)].

Effect of temperature. In a low-concentration solution, γ does not depend on the concentration but only on the temperature. In the interpretation of the temperature effect, it was established that g^* and g are independent of temperature. The measured partial differential quotient of the yield, according to temperature, for neutral water is as follows:

$$\left(\frac{\partial G}{\partial T}\right)_{c_s} = (g^* - g) \frac{d\gamma}{dT} \tag{6}$$

In a strongly acid solution, we obtain completely similarly:

$$\left(\frac{\partial G}{\partial T}\right)_{c_s} = (g^{*'} - g') \frac{d\gamma}{dT} \tag{7}$$

4. Calculation of the Temperature Dependence of the Radical Yields

Hochanadel and Chormley (Ref.5) determined the temperature dependence of the primary yields in an acid medium. Their results are compared here with eq.(7). For the purpose of our calculations it is assumed that a) ice behaves from the point of view of radiation chemistry as the "ice-like" groups of liquid water, and b) the ice matrix is a radical trap of the same effectiveness as the ions dissolved in water.

The three quantities on the right-hand side of eq.(7) are obtained in the following manner: The mole fraction of the "ice-like" water molecules must be taken from a two-phase water model. Wada's theory (Ref.13) gives the γ-value

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up to 10° C in steps of one degree and, between 10 and 20° C, in steps of every five degrees. For higher temperatures, the theoretical data by Némethy and Scheraga (Ref.12) are accepted; these calculations give the γ-values between 0 and 100° C at 10-degree intervals. The latter model, as mentioned, is a five-phase model; the water molecules of the three and four coordination are con- /180 sidered to be in the "ice-like" structure. Simultaneous application of the two theories is permitted by the fact that between 0° and 20° C, the temperature co-efficient of γ is obtained as an identical value from the two theories to an accuracy within 1%.

It has been mentioned that, according to our knowledge, the radical yield of frozen acid solutions has never been determined as 4.2° K, at which the H atoms usually are stable. Therefore, this yield cannot be given directly on the basis of the measurement of $g^{*\prime}$. However, the greater value of $g^{*\prime}$ with respect to g^{*} may be due to the looser atom distribution in the acid medium. The calculations by Dyne and Kennedy (Ref.15) show the yields to vary almost linearly with the radius of distribution of the H atoms. Therefore, the following relationship exists approximately:

$$g^{*\prime} \approx g^{*} + g^{\prime} - g$$
(8)

which, together with eqs.(1) and (5), yields a simple system with three un-knowns. The G, $G^{\prime}$, and G^{*} are measured values, with the first two taken from the paper by Hart and Platzman (Ref.17) and the last from the paper by Siegel et al. (Ref.8). The differential quotients of eq.(7) are approximated by the differential quotients of the examined temperature range.
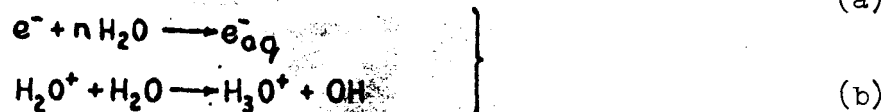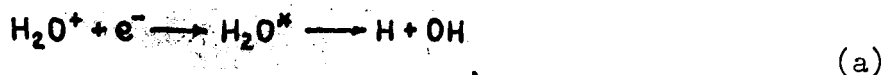
Table I contains the data used in the calculations, while Table II gives the measured and calculated values of the temperature coefficients of the radical yields.

5. Considerations on the Validity Limit of the Radical Diffusion Theory

Considering the extensive errors occurring in paramagnetic resonance measurements and the highly approximate nature of our calculations, the calcu-lated temperature coefficients of the OH radical yield show fairly good agree-ment with the measured values. The situation is often less favorable for the H atoms, where an agreement to only within one order of magnitude can be ob-tained. The available data are too few, and our calculations are too rough, to draw extensive conclusions from this fact. However, it is possible that, ac-cording to our present knowledge, the oxidizing agent formed in irradiated water is actually an OH radical (Ref.18) and no doubt is formed in clusters, whereas the reducing agent may appear in two forms, as a H atom and as a hydrated elec-tron (Ref.19), with the latter type probably reacting in a homogeneous distribu-tion. Thus, the model of radical diffusion definitely gives a more realistic picture of the reactions of OH radicals than of the reactions of the reducing agent.

On the other hand, the temperature affects the quality as well as the yield of the primary products. The fate of the thermolyzed electron may be of two

kinds: It is either recaptured by the positive parent molecule ion and the resulting excited water molecule decomposes into H and OH radicals (a) – this is the hypothesis of the theory of radical diffusion – or it migrates from the force field of the ion and becomes hydrated, after which the remaining H_2O^+ reacts with the neighboring water molecule (b). The two possibilities are represented by the following equations

$$H_2O^+ + e^- \longrightarrow H_2O^* \longrightarrow H + OH \qquad \text{(a)}$$

$$\left. \begin{array}{l} e^- + n\,H_2O \longrightarrow e^-_{aq} \\[4pt] H_2O^+ + H_2O \longrightarrow H_3O^+ + OH \end{array} \right\} \qquad \text{(b)}$$

The probability of the process (a) is equal to the probability of recapture of the thermolyzed electron. If the electron has an energy ϵ at the site of thermolysis, the probability of the recapture is

$$W = 1 - e^{-\frac{\epsilon}{kT}} \qquad (9)$$

The value of W agrees with the quotient $\dfrac{G_H}{G_{e^-} + G_H}$ found by Rabani and Stein (Ref.19b) to be 0.172. By substituting this on the left-hand side of eq.(9), the value of ϵ at T = 300°K will be 7.9×10^{-15} erg. Thus, at room temperature this is the energy of the thermolyzed electron in the Coulomb field of the positive ion.

Assuming that the value of ϵ does not vary with temperature, the value of W increases exponentially with decreasing temperature and becomes W = 1.000 at T = 4.2°K. In other words, at such a low temperature the process (a) takes place exclusively, and only H atoms with inhomogeneous distribution are formed. [Our assumption, according to which ϵ is only slightly dependent on temperature, can be substantiated as follows: The electrostatic energy of the electron depends on the product of the dielectric constant and the distance measured from the positive ion. According to Fröhlich and Platzman (Ref.20), the distance increases with an increase in dielectric relaxation time; according to the theory of dielectrics (Ref.21), the dielectric constant decreases. Although the relaxation time depends greatly on the temperature (Ref.22), the energy will still show only a slight temperature dependence.]

These results agree qualitatively very well with experience. It has been generally known that the yields of radiolysis of aqueous solutions exhibit a considerable isotope effect at room temperature. It is impossible to interpret this phenomenon by the theory of radical diffusion (Ref.15) since the variation in the isotope composition of the medium changes the constants of diffusion and reaction rate of the radicals exactly in a mutually compensating manner. Judeikis et al. (Ref.23) were unable to demonstrate an isotope effect in ice irradiated at 4.2°K; this indicates that, under the conditions of their measurement, the hypotheses of the radical diffusion theory correspond exactly to physical reality.

TABLE I /182

g^*_{OH}	G_{OH}	G'_{OH}
0.8^a	2.28^b	2.92^b
g^*_H	G_H	G'_H
0.9^a	2.78^b	3.65^b
$\gamma_{20°}$	$\left(\dfrac{\Delta\gamma}{\Delta T}\right)_{2-20°}$	$\left(\dfrac{\Delta\gamma}{\Delta T}\right)_{20-60°}$
0.35^c	$3.89 \cdot 10^{-3\,c}$	$2.6 \cdot 10^{-3\,d}$

The data used in the calculations:

$$a = [8]$$
$$b = [17]$$
$$c = [13]$$
$$d = [12].$$

TABLE II

	Calculated 2-20°	Measured (Ref. 5) 2-23°	Calculated 20-60°	Measured (Ref. 5) 23-65°
$\left(\dfrac{\Delta G'_{OH}}{\Delta T}\right) \cdot 10^3$	8.86	5.23	5.93	5.25
$\left(\dfrac{\Delta G'_H}{\Delta T}\right) \cdot 10^3$	11.2	3.82	7.50	3.58

Calculated and measured temperature coefficients of the yields of radicals.

Thus, in the first part of our work, the error committed was not so much due to the fact that the radical diffusion model was considered valid for ice without restriction but to the fact that this was done for water. In the calculation of the temperature coefficients, however, this error is negligible. There, basically nothing else was used than the measured values of the radical yields and the two theories of the water structure. The numerical agreement, if this can be used as a proof at all, confirms only the fact that, in liquid water, we must take into consideration molecular groups which show a behavior similar to

that of ice from the viewpoint of radiochemistry. Thus, our calculations cannot be considered as a proof for the theory of radical diffusion, but - exactly because of their semi-empirical nature - they are in agreement with the mechanism of the radiolysis of water according to Platzman (Ref.24).

REFERENCES

1. Hochanadel, C.J.: Comparative Effects of Radiation. John Wiley & Sons, New York, 1960.
2. Shinohara, K., Shida, R., and Saito, N.: J. Chem. Phys., Vol.35, p.1899, 1961.
3. Schiller, R.: J. Chim. Phys., Vol.59, p.267, 1962.
4. Schiller, R., Kósa-Somogyi, I., and Kiss, I.: Proc. 2nd Inter. Conf. Rad. Res. (to be published).
5. Hochanadel, C.J. and Chormley, J.A.: Radiation Res., Vol.16, p.653, 1962.
6. Mahlman, H.A.: J. Chem. Phys., Vol.32, p.601, 1960.
7. Burton, M. and Kurien, K.C.: J. Phys. Chem., Vol.63, p.899, 1959.
8. Siegel, S., Flournoy, J.M., and Baum, L.H.: J. Chem. Phys., Vol.34, p.1782, 1961.
9. Livingston, R. and Weinberger, A.J.: J. Chem. Phys., Vol.33, p.499, 1960.
10. Samoilow, O.J.: The Structure of Aqueous Electrolyte Solutions (Die Struktur von wässrigen Elektrolytlösungen), Leipzig, 1961.
11. Geszti, T. and Giber, J.: (to be published).
12. Némethy, G. and Scheraga, H.A.: J. Chem. Phys., Vol.36, p.3382, 1962.
13. Wada, G.: Bull. Chem. Soc. Japan, Vol.34, p.955, 1961.
14. Frank, H.S. and Wen, W.Y.: Discussion Faraday Soc., Vol.24, p.133, 1957.
15. Dyne, P.J. and Kennedy, J.M.: Can. J. Chem., Vol.36, p.1518, 1958.
16. Ganguly, A.K. and Magee, J.L.: J. Chem. Phys., Vol.25, p.129, 1956.
17. Hart, E.J. and Platzman, R.L.: Rad. Chem., Mech. of Radiobiol., Vol.I, pp.93-257, 1961.
18. Hummel, A. and Allen, A.O.: Radiation Res., Vol.17, p.302, 1962.
19a. Czapski, G. and Schwarz, H.A.: J. Phys. Chem., Vol.66, p.471, 1962.
19b. Rabani, J. and Stein, G.: J. Chem. Phys., Vol.37, p.1865, 1962.
20. Fröhlich, H. and Platzman, R.L.: Phys. Rev., Vol.95, p.1152, 1953.
21. Fröhlich, H.: Theory of Dielectrics. Clarendon, 1950.
22. Auty, R.P. and Cole, R.H.: J. Chem. Phys., Vol.20, p.1309, 1952.
23. Judeikis, H.S., Flournoy, J.M., and Siegel, S.: J. Chem. Phys., Vol.37, p.2272, 1962.
24. Platzman, R.L.: Basic Mechanisms in Radiobiology. Part II: Physical and Chemical Aspects, pp.22-50, Washington, 1953.